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(54) Title: ELASTOMERS AND PROCESS FOR THEIR MANUFACTURE			
(57) Abstract <p>A process for polymerizing ethylene, α-olefin and optionally diene monomers is disclosed. The process comprises the steps of contacting: (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α-olefin, (3) optionally, at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) an activator, and (5) a solvent. The process can be conducted in a single or multiple reactors, and if in multiple reactors, then the reactors can be configured in series or parallel. Solvent is removed from the polymer stream in an anhydrous, first stage solvent recovery operation such that the solids concentration of the product stream is increased by at least 100 percent. Additional solvent is removed in an anhydrous, second stage solvent recovery operation from the product of the first stage solvent recovery operation such that the solids concentration of the product stream is in excess of 65 weight percent.</p>			

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ELASTOMERS AND PROCESS FOR THEIR MANUFACTURE

This invention relates to elastomers. In one aspect, this invention relates to ethylene-propylene (EP) and ethylene-propylenediene monomer (EPDM) elastomers while in another aspect, this invention relates to a process for their manufacture. In yet another aspect, this invention relates to elastomers made by a process in which the catalyst is a metallocene complex, more particularly to a class of Group 4 metal complexes.

Metallocene complexes and methods for their preparation are disclosed in US-A-5,470,993 (published also as EP-A-705,269 and WO95/00526); USSN 545,403, filed July 3, 1990 (published also as EP-A-416,815); USSN 547,718, filed July 3, 1990 (published also as EP-A-468,651); USSN 702,475, filed May 20, 1991 (published also as EP-A-514,828); USSN 876,268, filed May 1, 1992, (published also as EP-A-520,732) and USSN 8,003, filed January 21, 1993 (published also as WO93/19104), as well as US-A-5,055,438, US-A-5,057,475, US-A-5,096,867, US-A-5,064,802, US-A-5,132,380.

The term "elastomer" was first defined in 1940 to mean synthetic thermosetting high polymers having properties similar to those of vulcanized natural rubber, that is, having the ability to be stretched to at least twice their original length and to retract very rapidly to approximately their original length when released. Representative of these "high polymers" were styrene-butadiene copolymer, polychloroprene, nitrite butyl rubber and ethylene-propylene terpolymers (also known as EPDM rubbers). The term "elastomer" was later extended to include uncrosslinked thermoplastic polyolefins, TPO's.

ASTM D 1566 defines various physical properties, and the test methods for measuring these properties, of rubbers. USP 5,001,205 (Hoel) provides an overview of the known elastomers comprising ethylene copolymerized with an α -olefin. As Hoel describes, commercially viable elastomers have various minimum properties, such as a Mooney viscosity no less than 10, a weight average molecular weight (Mw) no less than 110,000, a glass transition temperature below -40°C , and a degree of crystallinity no greater than 25 percent. USP 5,001,205 discloses a process for polymerizing high molecular weight elastomers using liquid phase polymerization in the presence of a metallocene/alumoxane (specifically, a bis(cyclopentadienyl) alumoxane) catalyst.

We have now discovered a process for the manufacture of ethylenepropylene and ethylene/ α -olefin/diene monomer polymers. In one embodiment, the process is characterized by the following steps:

- A. contacting in a first reactor (1) ethylene, (2) at least one C_3 - C_{20} aliphatic α -olefin, (3) optionally, at least one C_4 - C_{20} diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, and (5) a solvent, the first reactor operated such that a first product is produced at a solids concentration

of from 1 to 15 weight percent, based on the weight of the reaction mass in the first reactor;

- 5 B. contacting in a second reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally, at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, (5) a solvent, and (6) a product stream from the first reactor, the second reactor operated such that a second product is produced at a solids concentration of from 2 to 30 weight percent, based on the weight of the reaction mass in the second reactor;
- 10 C. removing a product stream from the second reactor;
- D. removing solvent from the product stream of the second reactor in an anhydrous, first stage solvent recovery operation such that the solids concentration of the product stream is increased by at least 100 percent; and
- 15 E. removing additional solvent in an anhydrous, second stage solvent recovery operation from the product of first stage solvent recovery operation such that the solids concentration of the product stream is in excess of 65 weight percent.

In another embodiment of this invention, the process is characterized by additional anhydrous solvent recovery operations in which the solids concentration of the final product is increased to greater than 99 weight percent. Preferably, the product of the first reactor has a weight average molecular weight greater than that of the product of the second reactor.

20 In yet another embodiment, the process is characterized by the following steps:

- 25 A. contacting in a first reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally, at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, and (5) a solvent, the first reactor operated such that a first product is produced at a solids concentration of from 1 to 30 weight percent, based on the weight of the reaction mass in the first reactor;
- 30 B. contacting in a second reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally, at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, (b) at least one activator, and (5) a solvent, the second reactor operated such that a second product is produced at a solids concentration of from 1 to 30 weight percent, based on the weight of the reaction mass in the second reactor;
- C. recovering a product stream from each of the first and second reactors, and then blending these individual product streams into a combined product stream;

D. removing solvent from the combined product stream in an anhydrous, first stage solvent recovery operation such that the solids concentration of the combined product stream is increased by at least 100 percent; and

E. removing additional solvent in an anhydrous, second stage solvent recovery operation from the combined product stream such that the solids concentration of the combined product stream is in excess of 65 weight percent.

In another embodiment of this invention, the process is further characterized by additional anhydrous solvent recovery operations in which the solids concentration of the final product is increased to greater than 99 weight percent. Preferably, the product of one reactor has a weight average molecular weight greater than that of the product of the other reactor.

Figure 1 is a diagrammatic representation of the two principal zones of the polymerization process of this invention.

Figure 2 is a diagrammatic representation of a single reactor embodiment of Zone I of Figure 1.

Figure 3 is a diagrammatic representation of an in-series dual reactor configuration of Zone I of Figure 1.

Figure 4 is a diagrammatic representation of an in-parallel dual reactor configuration of Zone I of Figure 1.

Figure 5 is a diagrammatic representation of four possible three-reactor configurations of Zone I of Figure 1.

Figure 6 is a diagrammatic representation of one embodiment of Zone II of Figure 1.

The elastomers made according to the new process disclosed herein are interpolymers of ethylene ($\text{CH}_2=\text{CH}_2$) with at least one comonomer selected from the group consisting of aliphatic C_3 - C_{20} α -olefins, conjugated dienes, and nonconjugated dienes. The term interpolymers includes copolymers, such as ethylene propylene (EP) copolymers, and terpolymers, such as EPDM, but is not intended to limit the elastomers made to only one or two monomers copolymerized with ethylene. Examples of the aliphatic C_3 - C_{20} α -olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. The α -olefin can also contain a cyclic structure such as cyclohexane or cyclopentane, resulting in an α -olefin such as 3-cyclohexyl-1-propene (allylcyclohexane) and vinyl-cyclohexane. Although not α -olefins in the classical sense of the term, certain cyclical olefins such as norbornene and related olefins can be used in place of some or all of the α -olefins.

Examples of nonconjugated dienes include aliphatic dienes such as 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,5-hexadiene, 1,6-heptadiene, 6-methyl-1,5-heptadiene, 1,6-octadiene, 1,7-octadiene, 7-methyl-1,6-octadiene, 1,13-tetradecadiene, and 1,19-eicosadiene; cyclic dienes such as

1,4-cyclohexadiene, bicyclo[2.2.1]hept-2,5-diene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, bicyclo[2.2.2]oct-2,5-diene, 4-vinylcyclohex-1-ene, bicyclo[2.2.2]oct-2,6-diene, 1,7,7-trimethylbicyclo-[2.2.1]hept-2,5-diene, dicyclopentadiene, methyltetrahydroindene, 5-allylbicyclo[2.2.1]hept-2-ene, and 1,5-cyclooctadiene; aromatic dienes
5 such as 1,4-diallylbenzene, 4-allyl-1H-indene; and trienes such as 2,3-diisopropenylidene-5-norbornene, 2-ethylidene-3-isopropylidene-5-norbornene, 2propenyl-2,5-norbornadiene, 1,3,7-octatriene, and 1,4,9-decatriene; with 5ethylidene-2-norbornene being a preferred nonconjugated diene.

Examples of conjugated dienes include butadiene, isoprene, 2,3dimethylbutadiene-1,3,
10 1,2-dimethylbutadiene-1,3, 1,4-dimethylbutadiene-1,3, 1ethylbutadiene-1,3, 2-phenylbutadiene-1,3, hexadiene-1,3, 4-methylpentadiene-1,3, 1,3-pentadiene ($\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$; commonly called piperylene), 3-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and 3-ethyl-1,3-pentadiene; with 1,3-pentadiene being a preferred conjugated diene.

Copolymers of ethylene and one aliphatic $\text{C}_3\text{-C}_{20}$ α -olefin or one diene (either
15 conjugated or nonconjugated) can be prepared using the process of this invention. Interpolymers of ethylene, at least one aliphatic $\text{C}_3\text{-C}_{20}$ α -olefin, and/or at least one diene (either conjugated or nonconjugated) can also be made by using this process. Exemplary copolymers include ethylene/propylene and ethylene/1-octene. Exemplary terpolymers include ethylene/propylene/1-octene, ethylene/propylene/5-ethylidene-2-norbornene,
20 ethylene/1-octene/5-ethylidene-2-norbornene, ethylene/propylene/1,3-pentadiene, and ethylene/1-octene/1,3-pentadiene. Exemplary tetrapolymers include ethylene/propylene/1-octene/diene (ENB) and ethylene/propylene/mixed dienes, such as ethylene/propylene/5-ethylidene-2-norbornene/piperylene. In addition, the elastomers made using the process of this invention can
25 include minor amounts, for instance, 0.05 - 0.5 percent by weight, of long chain branch enhancers, such as 2,5-norbornadiene (which is bicyclo[2.2.1]hepta-2,5-diene), diallylbenzene, 1,7-octadiene ($\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$), and 1,9-decadiene ($\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_6\text{CH}=\text{CH}_2$).

At a general minimum, the elastomers made by the process of this invention comprise at least 30, preferably at least 40 and more preferably at least 50 weight percent ethylene; at least 15,
30 preferably at least 20 and more preferably at least 25 weight percent of at least one α -olefin; and if present, preferably at least 0.1 and more preferably at least 0.5 weight percent of at least one conjugated or nonconjugated diene. At a general maximum, the elastomers made by the process of this invention comprise not more than 85, preferably not more than 80 and more preferably not more than 75 weight percent ethylene; not more than 70, preferably not more than 60 and more preferably
35 not more than 55 weight percent of at least one α -olefin; and not more than 20, preferably not more than 15 and more preferably not more than 12 weight percent of at least one of a conjugated or

nonconjugated diene. All weight percentages are based on weight of the elastomer which can be determined using any conventional method.

The polydispersity (molecular weight distribution or Mw/Mn) of the interpolymer elastomers generally ranges from 1.5, preferably from 1.8, and especially from 2.0 to 15, preferably to 10, and especially to 6.

Measurement of the polydispersity index is done according to the following technique: The polymers are analyzed by gel permeation chromatography (GPC) on a Waters 150°C high temperature chromatographic unit equipped with three linear mixed bed columns (Polymer Laboratories (10 micron particle size)), operating at a system temperature of 140°C. The solvent is 1,2,4-trichlorobenzene, from which about 0.5 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliter/minute and the injection size is 100 microliters.

The molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to derive the equation:

$$M_{\text{polyethylene}} = (a) (M_{\text{polystyrene}})^b$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, Mw, is calculated in the usual manner according to the formula:

$$M_w = \sum(w_i)(M_i)$$

where w_i and M_i are the weight fraction and molecular weight respectively of the i^{th} fraction eluting from the GPC column. Generally the Mw of the interpolymer elastomers ranges from 10,000, preferably from 20,000, more preferably from 40,000, and especially from 60,000 to 1,000,000, preferably to 800,000, more preferably to 600,000, and especially to 500,000.

The elastomers made by the process of this invention cover a range of viscosities, depending upon the molecular weight of the elastomer and optional post polymerization rheological modification. In general, the viscosity of elastomers is characterized by Mooney viscosity which is measured according to ASTM D 1646-89, using a shear rheometer at 125°C. The Mooney viscosity for the elastomers generally ranges from a minimum of 1, preferably 5, more preferably 10, and especially 15 to a maximum of 150, preferably 125, more preferably 100, and especially 80.

The density of the elastomers is measured according to ASTM D-792, and these densities range from 0.850 grams/cubic centimeter (g/cm^3), preferably from 0.853 g/cm^3 , and especially from 0.855 g/cm^3 , to 0.895 g/cm^3 , preferably to 0.885 g/cm^3 , and especially to 0.875 g/cm^3 .

Exemplary catalysts used in the process of this invention are metallocene complexes, and these catalysts and methods for their preparation are disclosed in USSN 545,403, filed July 3,

1990 (EP-A-416,815); USSN 702,475, filed May 20, 1991 (EP-A-514,828); as well as US-A-5,470,993; 5,374,696; 5,231,106; 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,321,106; 5,470,993; 5,486,632.

5 In USSN 720,041, filed June 24, 1991, (EP-A-514,828) certain borane derivatives of the foregoing metallocene complex catalysts are disclosed and a method for their preparation taught and claimed. In US-A-5,453,410, combinations of cationic metallocene complex catalysts with an alumoxane are disclosed as suitable olefin polymerization catalysts.

Preferred for use herein are catalyst compositions comprising:

10 a1) a metal complex corresponding to the formula: $ZLMX_pX'_q$, that has been or subsequently is rendered catalytically active by combination with an activating cocatalyst or by use of an activating technique,

wherein M is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +2, +3 or +4, bound in an η^5 bonding mode to L;

15 L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, Z. and L further may be substituted with from 1 to 8 substituents independently selected from the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamine, dihydrocarbylphosphino or silyl groups containing up to 20 nonhydrogen atoms;

20 Z is a divalent moiety bound to both L and M via σ -bonds, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and optionally, also comprising nitrogen, phosphorus, sulfur or oxygen;

X is an anionic or dianionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

25 X' independently each occurrence is a neutral Lewis base ligating compound, having up to 20 atoms;

p is 0, 1 or 2, and is two less than the formal oxidation state of M, with the proviso that when X is a dianionic ligand group, p is 1; and

q is 0, 1 or 2; said metal complex being rendered catalytically active by combination with an activating cocatalyst or use of an activating technique; or

30 a catalyst composition comprising a cationic complex a2) corresponding to the formula $(ZLM^*X_p^*A^-)$,

wherein: M^* is a metal of Group 4 of the Periodic Table of the Elements having an oxidation state of +3 or +4, bound in an η^5 bonding mode to L;

35 L is a cyclopentadienyl-, indenyl-, tetrahydroindenyl-, fluorenyl-, tetrahydrofluorenyl-, or octahydrofluorenyl- group covalently substituted with at least a divalent moiety, Z. and L further may be substituted with from 1 to 8 substituents independently selected from

the group consisting of hydrocarbyl, halo, halohydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, dihydrocarbylphosphino or silyl groups containing up to 20 nonhydrogen atoms;

Z is a divalent moiety bound to both L and M* via σ -bonds, said Z comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also optionally comprising nitrogen, phosphorus, sulfur or oxygen;

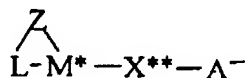
X* is an anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

p* is 0 or 1, and is three less than the formal oxidation state of M; and

A* is an inert, noncoordinating anion.

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any references to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

Zwitterionic complexes result from activation of a Group 4 metal diene complex, that is, complexes in the form of a metallocyclopentene wherein the metal is in the +4 formal oxidation state, by the use of a Lewis acid activating cocatalyst, especially tris(perfluoroaryl)borane compounds. These zwitterionic complexes are believed to correspond to the formula:



M is a Group 4 metal in the +4 formal oxidation state;

L and Z are as previously defined;

X** is the divalent remnant of the conjugated diene, X', formed by ring opening at one of the carbon to metal bonds of a metallocyclopentene; and

A⁻ is the moiety derived from the activating cocatalyst.

As used herein, the recitation "noncoordinating, compatible anion" means an anion which either does not coordinate to component a) or which is only weakly coordinated therewith remaining sufficiently labile to be displaced by a neutral Lewis base. A non-coordinating, compatible anion specifically refers to a compatible anion which when functioning as a charge balancing anion in the catalyst system of this invention, does not transfer an anionic substituent or fragment thereof to said cation thereby forming a neutral four coordinate metallocene and a neutral metal byproduct.

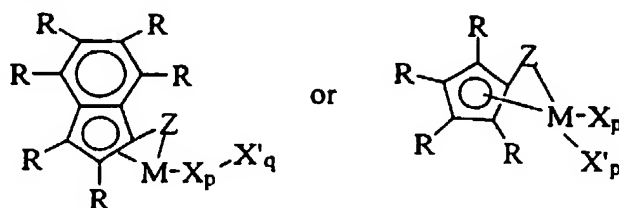
"Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerizations.

Preferred X' groups are phosphines, especially trimethylphosphine, triethylphosphine, triphenylphosphine and bis(1,2-dimethylphosphino)ethane; P(OR)₃, wherein R is as previously defined; ethers, especially tetrahydrofuran; amines, especially pyridine, bipyridine,

tetramethylethylenediamine (TMEDA), and triethylamine; olefins, and conjugated dienes having from

4 to 40 carbon atoms. Complexes including the latter X' groups include those wherein the metal is in the +2 formal oxidation state.

Preferred metal complexes a) used according to the present invention are complexes corresponding to the formula:



wherein:

R independently each occurrence is a group selected from hydrogen, hydrocarbyl, halohydrocarbyl, silyl, germyl and mixtures thereof, said group containing up to 20 nonhydrogen atoms;

M is titanium, zirconium or hafnium;

Z is a divalent moiety comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen, said moiety having up to 60 nonhydrogen atoms;

X and X' are as previously defined;

p is 0, 1 or 2; and

q is 0 or 1;

with the proviso that;

when p is 2, q is 0, M is in the +4 formal oxidation state, and X is an anionic ligand selected from the group consisting of halide, hydrocarbyl, hydrocarbyloxy,

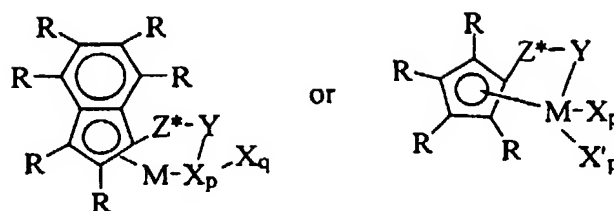
di(hydrocarbyl)amido, di(hydrocarbyl)phosphido, hydrocarbylsulfido, and silyl groups, as well as halo-, di(hydrocarbyl)amino-, hydrocarbyloxy- and di(hydrocarbyl)phosphino-substituted derivatives thereof, said X group having up to 20 nonhydrogen atoms,

when p is 1, q is 0, M is in the +3 formal oxidation state, and X is a stabilizing anionic ligand group selected from the group consisting of allyl,

2-(N,N-dimethylaminomethyl)phenyl, and 2-(N,N-dimethyl)aminobenzyl, or M is in the +4 formal oxidation state, and X is a divalent derivative of a conjugated diene, M and X together forming a metallocyclopentene group, and

when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is a neutral, conjugated or nonconjugated diene, optionally substituted with one or more hydrocarbyl groups, said X' having up to 40 carbon atoms and forming a π -complex with M.

More preferred coordination complexes a) used according to the present invention are complexes corresponding to the formula:



wherein

R independently each occurrence is hydrogen or C₁₋₆ alkyl;

5 M is titanium; Y is -O-, -S-, -NR^{*}-, -PR^{*}-;

Z^{*} is SiR^{*}₂, CR^{*}₂, SiR^{*}₂SiR^{*}₂, CR^{*}₂CR^{*}₂, CR^{*}=CR^{*}, CR^{*}₂SiR^{*}₂, or GeR^{*}₂;

R^{*} each occurrence is independently hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, and R^{*} having up to 20 nonhydrogen atoms, and optionally, two R^{*} groups from Z (when R^{*} is not
10 hydrogen), or an R^{*} group from Z and an R^{*} group from Y form a ring system;

p is 0, 1 or 2;

q is 0 or 1;

with the proviso that:

when p is 2, q is 0, M is in the +4 formal oxidation state, and X is independently each
15 occurrence methyl or benzyl,

when p is 1, q is 0, M is in the +3 formal oxidation state, and X is 2- (N,N-dimethyl)aminobenzyl); or M is in the +4 formal oxidation state and X is 1,4butadienyl, and

when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is 1,4-diphenyl-1,3-butadiene or 1,3-pentadiene. The latter diene is illustrative of unsymmetrical diene
20 groups that result in production of metal complexes that are actually mixtures of the respective geometrical isomers.

The complexes can be prepared by use of well known synthetic techniques. A preferred process for preparing the metal complexes is disclosed in US-A-5,491,246 (published also as WO96/34001). The reactions are conducted in a suitable noninterfering solvent at a temperature from
25 -100 to 300 °C, preferably from -78 to 100 °C, most preferably from 0 to 50°C. A reducing agent may be used to cause the metal M to be reduced from a higher to a lower oxidation state. Examples of suitable reducing agents are alkali metals, alkaline earth metals, aluminum and zinc, alloys of alkali metals or alkaline earth metals such as sodium/mercury amalgam and sodium/potassium alloy, sodium naphthalenide, potassium graphite, lithium alkyls, lithium or potassium alkadienyls, and Grignard
30 reagents.

Suitable reaction media for the formation of the complexes include aliphatic and aromatic hydrocarbons, ethers, and cyclic ethers, particularly branched-chain hydrocarbons such as

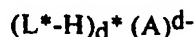
isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; aromatic and hydrocarbyl-substituted aromatic compounds such as benzene, toluene, and xylene, C₁₋₄ dialkyl ethers, C₁₋₄ dialkyl ether derivatives of (poly)alkylene glycols, and
 5 tetrahydrofuran. Mixtures of the foregoing are also suitable.

Suitable activating cocatalysts useful in combination with component al) are those compounds capable of abstraction of an X substituent from al) to form an inert, noninterfering counter ion, or that form a zwitterionic derivative of al). Suitable activating cocatalysts for use herein include
 10 perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluorophenyl)borane;

nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such
 15 compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, and ferritenium salts of compatible, noncoordinating anions. Suitable activating techniques include the use of bulk electrolysis (explained in more detail hereinafter). A combination of the foregoing activating
 20 cocatalysts and techniques may be employed as well. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, EP-A-468,651 (equivalent to USSN 07/547,718), EP-A-520,732 (equivalent to USSN 07/876,268), and EP-A-520,732 (equivalent to USSN 07/884,966 filed May 1, 1992). More particularly, suitable ion forming compounds useful as
 25 cocatalysts in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and a compatible, noncoordinating anion, A⁻.

Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined.

Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically
 30 unsaturated compounds or other neutral Lewis bases such as ethers or nitrites. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are well known, particularly such
 35 compounds containing a single boron atom in the anion portion, and are available commercially. Preferably such cocatalysts may be represented by the following general formula:



wherein:

L* is a neutral Lewis base;

(L*-H)⁺ is a Bronsted acid;

A^{d-} is a noncoordinating, compatible anion having a charge of $d-$, and d is an integer from 1-3.

More preferably A^{d-} corresponds to the formula: $[M'Q_4]^-$;

wherein:

5 M' is boron or aluminum in the formal +3 formal oxidation state; and

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstitutedhydrocarbyloxy, and halosubstituted silylhydrocarbyl radicals (including perhalogenated hydrocarbylperhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with
10 the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxy Q groups are disclosed in USP 5,296,433.

In a more preferred embodiment, d is 1, that is, the counter ion has a single negative charge and is A^- . Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

15 $(L^*-H)^+(BQ_4)^-$;

wherein:

L^* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated
20 hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

Most preferably, Q is at each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an
25 activating cocatalyst in the preparation of the improved catalysts of this invention are trisubstituted ammonium salts such as: trimethylammonium tetrakis(pentafluorophenyl) borate, triethylammonium tetrakis(pentafluorophenyl) borate, tripropylammonium tetrakis(pentafluorophenyl) borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate, tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
30 N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate, N,N-dimethylanilinium benzyltris(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(4-(t-butyl)dimethylsilyl)-2,3,5,6-tetrafluorophenyl) borate, N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2,3,5,6-tetrafluorophenyl) borate, N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate, N,N-diethylanilinium tetrakis(pentafluorophenyl)
35 borate, N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate, triethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)

borate, tripropylammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, tri(n-butyl)ammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, dimethyl(t-butyl)ammonium tetrakis (2,3,4,6-tetrafluorophenyl) borate, N,N-dimethylanilinium tetrakis (2,3,4,6-tetrafluorophenyl) borate, N,N-diethylanilinium tetrakis (2,3,4,6-tetrafluorophenyl) borate, and N,N-dimethyl-2,4,6-trimethylanilinium tetrakis (2,3,4,6-tetrafluorophenyl) borate; disubstituted ammonium salts such as: di-(i-propyl) ammonium tetrakis(pentafluorophenyl) borate, and dicyclohexylammonium tetrakis(pentafluorophenyl) borate; trisubstituted phosphonium salts such as: triphenylphosphonium tetrakis(pentafluorophenyl) borate, tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate; disubstituted oxonium salts such as: diphenyloxonium tetrakis(pentafluorophenyl) borate, di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and di(2,6-dimethylphenyl) oxonium tetrakis (pentafluorophenyl) borate; disubstituted sulfonium salts such as: diphenylsulfonium tetrakis(pentafluorophenyl) borate, di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and bis(2,6-dimethylphenyl)sulfonium tetrakis(pentafluorophenyl) borate.

Preferred (L*-H)⁺ cations are N,N-dimethylanilinium and tributylammonium.

Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:



wherein:

Ox^{e+} is a cationic oxidizing agent having a charge of e+;

e is an integer from 1 to 3; and

Ad⁻ and d are as previously defined.

Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag⁺ or Pb²⁺. Preferred embodiments of Ad⁻ are those anions previously defined with respect to the Bronsted acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl)borate.

Another suitable ion forming, activating cocatalyst comprises a compound which is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula:

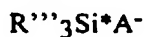


wherein:

⊕⁺ is a C₁₋₂₀ carbenium ion; and

A⁻ is as previously defined. A preferred carbenium ion is the trityl cation, that is, triphenylmethylum.

A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:



wherein:

5

R''' is C_{1-10} hydrocarbyl, and A^- is as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate and ether substituted adducts thereof. Silylium salts have been previously generically disclosed in J. Chem. Soc. Chem. Comm. 1993, 383-384, as well as Lambert, J.B., et al, Organometallics, 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is claimed in US-A-5,625,087.

Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in USP 5,296,433.

The technique of bulk electrolysis involves the electrochemical oxidation of the metal complex under electrolysis conditions in the presence of a supporting electrolyte comprising a noncoordinating, inert anion. In the technique, solvents, supporting electrolytes and electrolytic potentials for the electrolysis are used such that electrolysis byproducts that would render the metal complex catalytically inactive are not substantially formed during the reaction. More particularly, suitable solvents are materials that are (i) liquids under the conditions of the electrolysis (generally temperatures from 0 to 100°C), (ii) capable of dissolving the supporting electrolyte, and (iii) inert. "Inert solvents" are those that are not reduced or oxidized under the reaction conditions employed for the electrolysis. It is generally possible in view of the desired electrolysis reaction to choose a solvent and a supporting electrolyte that are unaffected by the electrical potential used for the desired electrolysis. Preferred solvents include diduorobenzene (all isomers), dimethoxyethane (DME), and mixtures thereof.

The electrolysis may be conducted in a standard electrolytic cell containing an anode and cathode (also referred to as the working electrode and counterelectrode respectively). Suitable materials of construction for the cell are glass, plastic, ceramic and glass-coated metal. The electrodes are prepared from inert conductive materials, by which are meant conductive materials that are unaffected by the reaction mixture or reaction conditions. Platinum or palladium are preferred inert conductive materials. Normally an ion permeable membrane such as a fine glass grit separates the cell into separate compartments, the working electrode compartment and counterelectrode compartment. The working electrode is immersed in a reaction medium comprising the metal complex to be activated, solvent, supporting electrolyte, and any other materials desired for moderating the

electrolysis or stabilizing the resulting complex. The counterelectrode is immersed in a mixture of the solvent and supporting electrolyte. The desired voltage may be determined by theoretical calculations or experimentally by sweeping the cell using a reference electrode such as silver electrode immersed in the cell electrolyte. The background cell current, the current draw in the absence of the desired electrolysis, is also determined. The electrolysis is completed when the current drops from the desired level to the background level. In this manner, complete conversion of the initial metal complex can be easily detected.

Suitable supporting electrolytes are salts comprising a cation and a compatible, noncoordinating anion, A^- . Preferred supporting electrolytes are salts corresponding to the formula G^+A^- ;

wherein:

G^+ is a cation which is nonreactive towards the starting and resulting complex, and A^- is as previously defined.

Examples of cations, G^+ , include tetrahydrocarbyl substituted ammonium or phosphonium cations having up to 40 nonhydrogen atoms. Preferred cations are the tetra(n-butylammonium)- and tetraethylammonium- cations.

During activation of the complexes of the present invention by bulk electrolysis the cation of the supporting electrolyte passes to the counterelectrode and A^- migrates to the working electrode to become the anion of the resulting oxidized product. Either the solvent or the cation of the supporting electrolyte is reduced at the counterelectrode in equal molar quantity with the amount of oxidized metal complex formed at the working electrode. Preferred supporting electrolytes are tetrahydrocarbylammonium salts of tetrakis(perfluoroaryl) borates having from 1 to 10 carbons in each hydrocarbyl or perfluoroaryl group, especially tetra(n-butylammonium)tetrakis(pentafluorophenyl) borate.

A further recently discovered electrochemical technique for generation of activating cocatalysts is the electrolysis of a disilane compound in the presence of a source of a noncoordinating compatible anion. All of the foregoing techniques are more fully disclosed and claimed in US-A-5,372,682 (published also as EP-656,075 and WO95/00683). In as much as the activation technique ultimately produces a cationic metal complex, the amount of such resulting complex formed during the process can be readily determined by measuring the quantity of energy used to form the activated complex in the process.

Alumoxanes, especially methylalumoxane or triisobutylaluminum modified methylalumoxane are also suitable activators and may be used for activating the present metal complexes.

A most preferred activating cocatalyst is tris(pentafluorophenyl)borane.

The molar ratio of metal complex: activating cocatalyst employed preferably ranges from 1:1000 to 2:1, more preferably from 1:5 to 1.5:1, most preferably from 1:2 to 1:1.

Highly preferred metal complexes are:

tetramethylcyclopentadienyl complexes:

- 5 (n-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(n-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
(n-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- 10 (n-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
(n-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
(t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-
- 15 pentadiene,
(t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
(t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
(t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
- 20 (cyclododecylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(cyclododecylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
(cyclododecylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- 25 (cyclododecylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
(cyclododecylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
(2,4,6-trimethylanilido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(2,4,6-trimethylanilido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
- 30 (2,4,6-trimethylanilido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
(2,4,6-trimethylanilido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
(2,4,6-trimethylanilido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
(1-adamantylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
- 35 1,4-diphenyl-1,3-butadiene,
(1-adamantylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene.

- (1-adamantylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 5 (t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 10 (t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 15 (n-butylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (n-butylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 20 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 25 (cyclododecylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methyl-indenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 30 1,3-pentadiene,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methylindene)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 35 (1-adamantylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

- (1-adamantylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 5 (1-adamantylamido)diisopropoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 10 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 15 (cyclododecylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 20 (2,4,6-trimethylanilido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 25 (2,4,6-trimethylanilido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl'
 (1-adamantylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene.
 30 (1-adamantylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)dimethoxy(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 35 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,

- (n-butylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (n-butylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 5 (cyclododecylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 10 (cyclododecylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 15 1,3-pentadiene, (2,4,6-trimethylanilido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium
 (III) 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II)
 20 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dimethyl,
 25 (1-adamantylamido)ethoxymethyl(η^5 -tetramethylcyclopentadienyl)silanetitanium (IV) dibenzyl,
2-methylindenyl complexes:
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-
 butadiene,
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 30 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 35 (n-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

- (n-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 5 (cyclododecylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 10 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (1-adamantylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 15 (1-adamantylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 20 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl
 25 1,3-butadiene,
 (n-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl,
 (n-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 30 (n-butylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4
 diphenyl-1,3-butadiene,
 (cyclododecylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-
 pentadiene,
 35 (cyclododecylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-
 (N,N-dimethylamino)benzyl,

- (cyclododecylamido)diisopropoxy(η^5 -2-methylindenyl)-silanetitanium (IV)dimethyl,
 (cyclododecylamido)diisopropoxy(η^5 -2-methylindenyl)-silanetitanium (IV)dibenzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methyl-indenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene,
- 5 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-
 (N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (IV)dimethyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (IV)dibenzyl,
- 10 (1-adamantylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4diphenyl-1,3-butadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3
 pentadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N
 dimethylamino)benzyl,
- 15 (1-adamantylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (IV)dimethyl,
 (1-adamantylamido)diisopropoxy(η^5 -2-methylindenyl)silanetitanium (IV)dibenzyl,
 (n-butylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl1,3-butadiene,
 (n-butylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N
 20 dimethylamino)benzyl,
 (n-butylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium(II) 1,4diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-
 25 pentadiene,
 (cyclododecylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl,
 (cyclododecylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
- 30 (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4
 diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N
 dimethylamino)benzyl,
- 35 (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV)dimethyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV)dibenzyl,

- (1-adamantylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- 5 (1-adamantylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)dimethoxy(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-diphenyl
 1,3-butadiene,
 (n-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
- 10 (n-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (III) 1,4-
 diphenyl-1,3-butadiene,
- 15 (cyclododecylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-
 (N,N-dimethylamino)benzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV)dimethyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV)dibenzyl,
- 20 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-
 dimethylamino)benzyl,
- 25 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV)dimethyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV)dibenzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,4diphenyl-1,3-butadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (III) 2-(N,N-
 30 dimethylamino)benzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methylindenyl)silanetitanium (IV) dibenzyl,

2,3-dimethylindenyl complexes:

- 35 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl1,3-butadiene,
 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,

- (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)-silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 5 (n-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)-silanetitanium (III) 2-(N,N
 dimethylamino)benzyl,
 (n-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 10 (cyclododecylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N
 dimethylamino)benzyl,
 15 (cyclododecylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dimethyl,
 (cyclododecylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dibenzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 20 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2
 (N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dimethyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dibenzyl,
 (1-adamantylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4diphenyl-1,3-butadiene,
 25 (1-adamantylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N
 dimethylamino)benzyl,
 (1-adamantylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dimethyl,
 (1-adamantylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dibenzyl,
 30 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl
 1,3-butadiene,
 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 35 (t-butylamido)dimethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4diphenyl-1,3-butadiene.

- (n-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl
 (n-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 5 (n-butylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (III) 2-
 10 (N,N-dimethylamino)benzyl,
 (cyclododecylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (IV) dimethyl,
 (cyclododecylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)-silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 15 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 20 (1-adamantylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 25 (1-adamantylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)diisopropoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 30 (n-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 35 (cyclododecylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

- (cyclododecylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dimethyl,
 (cyclododecylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dibenzyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene,
 5 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-
 (N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dimethyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dibenzyl,
 10 (1-adamantylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene,
 (1-adamantylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-
 (N,N-dimethylamino)benzyl,
 15 (1-adamantylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dimethyl,
 (1-adamantylamido)dimethoxy(η^5 -2,3-dimethylindenyl)silanetitanium (IV)dibenzyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)-silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N
 20 dimethylamino)benzyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 25 (cyclododecylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-
 (N,N-dimethylamino)benzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 30 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II)
 1,3-pentadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III)
 35 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,

(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2,3-dimethylindenyl)silanetitanium (IV) dibenzyl,

3-methylindenyl complexes:

(t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,

- (2,4,6-trimethylanilido)dimethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (2,4,6-trimethylanilido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
- (2,4,6-trimethylanilido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
- 5 (1-adamantylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl 1,3-butadiene,
- (1-adamantylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
- (1-adamantylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- 10 (1-adamantylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
- (1-adamantylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
- (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3butadiene,
- (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
- (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N
- 15 dimethylamino)benzyl,
- (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
- (t-butylamido)dimethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
- (n-butylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl 1,3-butadiene,
- 20 (n-butylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
- (n-butylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (II) 2-(N,N-dimethylamino)benzyl,
- (n-butylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
- (n-butylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
- (cyclododecylamido)diisopropoxy(η^5 -3-methylindenyl)-silanetitanium (II) 1,4-
- 25 diphenyl-1,3-butadiene,
- (cyclododecylamido)diisopropoxy(η^5 -3-methylindenyl)-silanetitanium (III) 1,3-pentadiene.
- (cyclododecylamido)diisopropoxy(η^5 -3-methylindenyl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (cyclododecylamido)diisopropoxy(η^5 -3-methylindenyl)-silanetitanium (IV) dimethyl,
- 30 (cyclododecylamido)diisopropoxy(η^5 -3-methylindenyl)-silanetitanium (IV) dibenzyl,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (II) 1 4-diphenyl-1,3-butadiene,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (III) 2-
- 35 (N,N-dimethylamino)benzyl,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,

- (2,4,6-trimethylanilido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
(1-adamantylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(1-adamantylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
(1-adamantylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-
5 dimethylamino)benzyl,
(1-adamantylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
(1-adamantylamido)diisopropoxy(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
(n-butylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl
1,3-butadiene,
10 (n-butylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
(n-butylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
(n-butylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
(n-butylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
(cyclododecylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
15 (cyclododecylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
(cyclododecylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-
dimethylamino)benzyl,
(cyclododecylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
(cyclododecylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
20 (2,4,6-trimethylanilido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-
1,3-butadiene,
(2,4,6-trimethylanilido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
(2,4,6-trimethylanilido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-
dimethylamino)benzyl,
25 (2,4,6-trimethylanilido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
(2,4,6-trimethylanilido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV)
dibenzyl,
(1-adamantylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,4-
diphenyl-1,3-butadiene,
30 (1-adamantylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (II) 1,3-
pentadiene,
(1-adamantylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-
dimethylamino)benzyl,
(1-adamantylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
35 (1-adamantylamido)dimethoxy(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
(n-butylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene.

- (n-butylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N dimethylamino)benzyl,
 (n-butylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
 5 (n-butylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-
 10 (N,N-dimethylamino)benzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 15 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,
 20 (1-adamantylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (III) 2-(N,N dimethylamino)benzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dimethyl,
 25 (1-adamantylamido)ethoxymethyl(η^5 -3-methylindenyl)silanetitanium (IV) dibenzyl,

2-methyl-3-ethylindenyl complexes:

- (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 30 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 35 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium, (II) 1,4-diphenyl-1,3-butadiene.

- (n-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 5 (n-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 10 (cyclododecylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II)
 15 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 20 (2,4,6-trimethylanilido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (1-adamantylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 25 (1-adamantylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)-silanetitanium (II) 1,4diphenyl-1,3-butadiene,
 30 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 35 (n-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

- (n-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 5 (n-butylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 10 (cyclododecylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)-silanetitanium, (III) 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)-silanetitanium (IV) dimethyl,
 (cyclododecylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)-silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 15 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 20 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl'
 (1-adamantylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 25 (1-adamantylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)diisopropoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 30 (n-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 35 (cyclododecylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,

- (cyclododecylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (cyclododecylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
- (cyclododecylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
- 5 (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
- (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
- (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III)
- 10 2-(N,N-dimethylamino)benzyl,
- (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
- (2,4,6-trimethylanilido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
- (1-adamantylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-
- 15 diphenyl-1,3-butadiene,
- (1-adamantylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
- (1-adamantylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (1-adamantylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
- 20 (1-adamantylamido)dimethoxy(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
- (n-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
- (n-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
- 25 (n-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (n-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
- (n-butylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV)
- 30 dibenzyl,
- (cyclododecylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
- (cyclododecylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
- 35 (cyclododecylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

- (cyclododecylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
- 5 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- 10 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (II)
- 15 1,3-pentadiene,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dimethyl,
- 20 (1-adamantylamido)ethoxymethyl(η^5 -2-methyl-3-ethylindenyl)silanetitanium (IV) dibenzyl,

2,3,4,6-tetramethylindenyl complexes

- (t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium] (II) 1,4diphenyl-1,3-butadiene,
- 25 (t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 1,3-pentadiene,
 (t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
- 30 (n-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,4diphenyl-1,3-butadiene,
 (n-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)-silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (n-butylarnido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
- 35 (n-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)

- 1,4-diphenyl-1,3-butadiene,
(cyclododecylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
1,3-pentadiene,
(cyclododecylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 2-
- 5 (N,N-dimethylamino)benzyl,
(cyclododecylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
(cyclododecylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
(2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
1,4-diphenyl-1,3-butadiene,
- 10 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
(2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III)
2-(N,N-dimethylamino)benzyl,
(2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
(2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl.
- 15 (1-adamantylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
1,4-diphenyl-1,3-butadiene,
(1-adamantylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
1,3-pentadiene,
(1-adamantylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 2-
- 20 (N,N-dimethylamino)benzyl,
(1-adamantylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV)
dimethyl,
(1-adamantylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV)
dibenzyl,
- 25 (t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
(t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 2-(N,N-
- 30 dimethylamino)benzyl,
(t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
(t-butylamido)dimethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
(n-butylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
1,4-diphenyl-1,3-butadiene,
- 35 (n-butylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,

- (n-butylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (n-butylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
- (n-butylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV)
- 5 dibenzyl,
- (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
- (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
- 10 (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
- (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
- 15 1,4-diphenyl-1,3-butadiene,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III)
- 2-(N,N-dimethylamino)benzyl,
- (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
- 20 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl
- (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
- 1,4-diphenyl-1,3-butadiene,
- (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
- (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III)
- 25 2-(N,N-dimethylamino)benzyl,
- (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
- (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
- (n-butylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
- 30 (n-butylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
- (n-butylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- (n-butylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV)
- 35 dimethyl,
- (n-butylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV)

- dibenzyl,
 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
 5 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
 10 (II) 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
 (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
 (III) 2-(N,N-dimethylamino)benzyl,
 15 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
 (IV) dimethyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
 (IV) dibenzyl,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
 20 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
 1,3-pentadiene,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 25 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
 30 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
 35 (II) 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium

- (II) 1,3-pentadiene,
(cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- (III) 2-(N,N-dimethylamino)benzyl,
(cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- 5 (IV) dimethyl,
(cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- (IV) dibenzyl,
(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- (II) 1,4-diphenyl-1,3-butadiene,
- 10 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- (II) 1,3-pentadiene,
(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- (III) 2-(N,N-dimethylamino)benzyl,
(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- 15 (IV) dimethyl,
(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- (IV) dibenzyl,
(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium
- (II) 1,4-diphenyl-1,3-butadiene,
- 20 (1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (II) 1,3-pentadiene,
(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (III)
- 2-(N,N-dimethylamino)benzyl,
(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dimethyl, and
(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6-tetramethylindenyl)silanetitanium (IV) dibenzyl
- 25 2,3,4,6,7-pentamethylindenyl complexes:
(t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
- 30 (t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
(t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
(t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
(n-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,4-
- 35 diphenyl-1,3-butadiene,
(n-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,

- (n-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethyl (η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 5 (cyclododecylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,3-pentadiene,
 (cyclododecylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 10 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 15 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 20 (1-adamantylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 25 (1-adamantylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,4-
 diphenyl-1,3-butadiene,
 (t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 30 (t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III) 2-
 (N,N-dimethylamino)benzyl,
 (t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (t-butylamido)dimethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 35 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,

- (n-butylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 5 (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,3-pentadiene,
 (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 10 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 15 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,3-pentadiene,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 20 (2,4,6-trimethylanilido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 25 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (1-adamantylamido)diisopropoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (n-butylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 30 (n-butylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (n-butylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 35 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,

- (cyclododecylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 5 (cyclododecylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,3-pentadiene,
 10 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (2,4,6-trimethylanilido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 15 1,4-diphenyl-1,3-butadiene,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 20 (1-adamantylamido)dimethoxy(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium
 (IV) dibenzyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,4-diphenyl-1,3-butadiene,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,3-pentadiene,
 25 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (n-butylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 30 1,4-diphenyl-1,3-butadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)
 1,3-pentadiene,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)
 2-(N,N-dimethylamino)benzyl,
 35 (cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,
 (cyclododecylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,

(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)

1,4-diphenyl-1,3-butadiene,

(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)

1,3-pentadiene,

5 (2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)

2-(N,N-dimethylamino)benzyl,

(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl,

(2,4,6-trimethylanilido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl,

(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II) 1,4-diphenyl-

10 1,3-butadiene,

(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (II)

1,3-pentadiene,

(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (III)

2-(N,N-dimethylamino)benzyl,

15 (1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dimethyl, and

(1-adamantylamido)ethoxymethyl(η^5 -2,3,4,6,7-pentamethylindenyl)silanetitanium (IV) dibenzyl.

In general, the polymerization according to the present invention may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky Sinn type
 20 polymerization reactions, that is, temperatures from 0 to 250°C and pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other polymerization process conditions may be employed if desired, however, solution polymerization process conditions, especially continuous solution polymerization process conditions, are preferred. A support may be employed but preferably the catalysts are used in a homogeneous manner, that is, they are dissolved in
 25 the solvent. Of course, the active catalyst system can form *in situ* if the catalyst and its cocatalyst components are added directly to the polymerization process and a suitable solvent or diluent (such as hexane or iso-octane) including condensed monomer, are also used. Preferably the active catalyst is formed separately in a suitable solvent, such as in a slip stream, prior to adding it to the polymerization mixture.

30 As previously mentioned, the present catalyst system is particularly useful in the preparation of EP and EPDM copolymers in high yield and productivity. The process employed may be either a solution or slurry process both of which are previously known in the art. Kaminsky, J. Poly. Sci., Vol. 23, pp. 2151-64 (1985) reported the use of a soluble bis(cyclopentadienyl) zirconium dimethyl-alumoxane catalyst system for solution polymerization of EP and EPDM elastomers. USP
 35 5,229,478 disclosed a slurry polymerization process utilizing similar bis(cyclopentadienyl) zirconium based catalyst systems.

In general terms, it is desirable to produce such EP and EPDM elastomers under conditions of increased reactivity of the diene monomer component. The reason for this was explained in USP 5,229,478 in the following manner, which still remains true despite the advances attained in such reference. A major factor affecting production costs and hence the utility of an EPDM is the diene monomer cost. The diene is a more expensive monomer material than ethylene or propylene. Further, reactivity of diene monomers with previously known metallocene catalysts is lower than that of ethylene and propylene. Consequently, to achieve the requisite degree of diene incorporation to produce an EPDM with an acceptably fast cure rate, it has been necessary to use a diene monomer concentration which, expressed as a percentage of the total concentration of monomers present, is in substantial excess compared to the percentage of diene desired to be incorporated into the final EPDM product. Since substantial amounts of unreacted diene monomer must be recovered from the polymerization reactor effluent for recycle, the cost of production is increased unnecessarily.

Further adding to the cost of producing an EPDM is the fact that, generally, the exposure of an olefin polymerization catalyst to a diene, especially the high concentrations of diene monomer required to produce the requisite level of diene incorporation in the final EPDM product, often reduces the rate or activity at which the catalyst will cause polymerization of ethylene and propylene monomers to proceed. Correspondingly, lower throughputs and longer reaction times have been required, compared to the production of an ethylene-propylene copolymer elastomer or other α -olefin copolymer elastomer.

Advantageously, a metallocene catalyst, especially a monocyclopentadienyl or -indenyl metallocene, is chosen that allows for increased diene reactivity which results in the preparation of EPDM polymers in high yield. For example, the monocyclopentadienyl and indenyl metallocene catalysts described previously, perform well in this respect. Additionally, these catalyst systems achieve the economical production of fast curing EPDM polymers with diene contents of up to 20 weight percent or higher.

As a further illustration of the solution polymerization embodiment of this invention, reference is made to the figures. Optional aspects of the embodiments described in the figures are depicted with a dashed line.

In Figure 1, the process is illustrated as comprising two principal zones or steps, that is, (1) polymer formation and (2) polymer recovery, and solvent and unreacted monomer recovery and recycle or disposal. In the first zone, the process reagents are admixed in proper proportion and under appropriate conditions to form the desired polymer while in the second zone, the desired polymer is separated from unreacted monomer and solvent. The polymer is recovered for storage and/or use, the solvent is recycled, and the unreacted monomers are either recycled or disposed (the choice being dependent upon various factors such as monomer concentration, and monomer price).

Figure 2 illustrates a single reactor embodiment of Zone I of Figure 1. In this embodiment, the process reagents, that is, ethylene, one or more α -olefins, optionally one or more dienes, solvent, catalyst and optionally a molecular weight regulator (such as hydrogen), are fed to a single reaction vessel of any suitable design, such as stirred tank or loop. The process reagents are contacted within the reaction vessel under appropriate conditions to form the desired polymer, and then the output of the reactor is transferred to Zone II. All of the output can be transferred at one time to Zone II (as in the case of a single pass or other batch reactor), or it can be in the form of a bleed stream which forms only a part, typically a minor part, of the reaction mass (as in the case of a continuous process reactor in which an output stream is bled from the reactor at the same rate at which reagents are added to maintain the polymerization at steady-state conditions). Recovered solvent and unreacted monomers from Zone II can be recycled back to Zone I.

Figure 3 illustrates a preferred embodiment of Zone I of Figure 1 in which two reactors are configured and operated in series, that is, the output of one reactor is fed to the second reactor. The reactors can be the same or different but preferably, each is the same and each is a loop reactor. The reactors can be operated in like or different modes, but preferably the first reactor is operated in such a manner that the formation of the high molecular weight fraction of the desired polymer is promoted while the second reactor (that is, the reactor that receives as a feed the output from the first reactor) is operated in such a manner that the formation of the low molecular weight fraction of the desired polymer is promoted.

The temperature difference between the first and second reactor influences the molecular weight distribution (MWD) of the final product, such that the greater the temperature difference, the broader the MWD. While the operating temperature of each reactor will depend upon a host of factors, such as the α -olefin(s), the diene(s) (if any), the catalyst, the solvent, equipment and equipment design, pressure, flow rate and turbulence, the relative amounts of the reagents, and desired product properties, a typical operating temperature for the first reactor is between 65 and 90°C. and a typical operating temperature for the second reactor is between 85 and 120°C. The residence time of the reactants in the individual reactors will also depend upon these factors, but a typical residence time for the reactants in each reactor is between 2 and 90 minutes.

Ethylene, α -olefin, diene (if any), solvent and, optionally, hydrogen are blended by any convenient means in desired proportion, and then the blend is introduced into the first reactor, that is, the reactor whose output is used as a feed for the other or second reactor. Catalyst is typically introduced into the first reactor apart from the other reagents. Preferably, the first and second reactors are operated on a continuous basis such that as output from the first reactor is withdrawn as feed for the second reactor, additional reagents are added to the first reactor to maintain the reaction mass in a steady-state, that is, a relatively constant and proportional concentration of ethylene, α -olefin, diene (if any), solvent, catalyst and molecular weight regulator (if any).

The first and second reactors are in fluid communication with one another, typically connected by one or more conduits. These conduits are typically equipped with one or more mixers (to promote a homogeneous blending of the reaction mass).

As with the first reactor, ethylene, α -olefin, diene (if any), solvent and, optionally, hydrogen are blended by any convenient means in desired proportion, and then the blend is introduced into the second reactor, that is, the reactor that receives as a feed the output from the other or first reactor. Likewise, catalyst (the same as or different from the catalyst used in the first reactor) is typically introduced into the second reactor apart from the other reagents. The output from the first reactor typically contains from 1 to 30 weight percent solids (that is, polymer), and it either can be fed to the second reactor apart from the other reagents, or it can first be blended with one or more of the other reagents prior to its introduction into the second reactor. The output from the second reactor typically contains between 8 to 30 weight percent solids, and it is transferred to Zone II in which the desired polymer product is separated from the solvent and unreacted monomers, and the latter (that is, solvent and unreacted monomers) are individually either recycled to Zone I or disposed in a safe and environmentally acceptable manner.

Figure 4 illustrates a preferred embodiment of Zone I of Figure 1 in which two reactors are configured and operated in parallel, that is, neither reactor produces a feed for the other reactor. Here too, the reactors can be the same or different, but preferably each is the same as the other and each is a loop reactor. The reactors can be operated in like or different modes, but preferably one reactor is operated in such a manner that the formation of the high molecular weight fraction of the desired polymer is promoted while the other reactor is operated in such a manner that the formation of the low molecular weight fraction of the desired polymer is promoted. Preferably each reactor is operated in a steady-state mode with an operating temperature and reagent residence time similar to that of the reactors configured and operated in series. Mixers, pumps and other such equipment are employed as desired.

The output from each reactor typically contains between about 1 and about 30 weight percent solids. While the output from the individual reactors can be routed separately to Zone II, typically the output from each reactor is mixed with the other prior to routing to Zone II.

Figure 5 illustrates four possible configurations for embodiments of this invention comprising three reactors. Configuration A depicts three reactors in series with the output from the first reactor serving as a feed for the second reactor, and the output from the second reactor serving as a feed for the third reactor. Configuration B depicts three reactors in parallel in which none of the reactors use as a feed the output from one of the other reactors. Configuration C depicts three reactors in which the two reactors are in series, and the two in series are in parallel with the third. Configuration D depicts three reactors in which two are in parallel, and the two in parallel are in series

with the third. Similar configurations can be drawn for embodiments comprising four or more reactors.

Figure 6 illustrates one embodiment of Zone II of this invention. Reaction product, that is the ultimate EP or EPDM product comprising both the high and low molecular weight fractions, is removed from Zone I (which ends at the point(s) at which reaction product is no longer routed to another reactor) to a first stage solvent recovery system. The reaction product is typically between 8 and 30 weight percent solids, and comprises EP or EPDM copolymer, solvent, unreacted comonomers, catalyst and catalyst residue, and residual amounts of hydrogen. Recovery of the copolymer requires its separation from these other components and according to the process of this invention, this is accomplished without the use of steam stripping, that is, essentially under anhydrous conditions (although minor amounts of water may be present in the reaction product from other sources, for instance, as a deactivator for the borane component of the catalyst).

The reaction product or product stream from Zone I is typically at a temperature between 90 and 120°C (the operating temperature of the second reactor in a two reactor configuration) and for embodiments in which a flash devolatilizer is the equipment of the first stage solvent recovery zone, the temperature of this stream is preferably raised to between 210 and 250°C by routing the stream through a series of heat exchangers. In the devolatilizer the product stream is subjected to a sudden pressure drop of at least 50 percent which results in a majority of the solvent and unreacted monomers to flash off for eventual separation, recycle and purification or disposal. The remaining portion of the product stream, that is, the condensed or polymer-containing phase, is discharged, typically through a gear pump which is operated under a positive pressure (for instance, from 5 to 100 psig (35 to 700 kPa)), into the second stage solvent recovery zone, which is, for instance, a vacuum extruder or other vacuum vessel, or a thermal dryer. At this point, the solids content of the product stream has increased over 100 percent, for instance, to between 20 and 80 weight percent.

The second stage recovery zone is operated under conditions in which the solids content of the product stream is increased to over 99 weight percent before it is transferred in a molten state to the polymer isolation zone. This zone can comprise any equipment in which the polymer product is finished for use, storage and/or shipping, for instance, a pelletizer or baler.

In another embodiment of this invention, the process comprises more than two anhydrous solvent recovery operations in which the solids concentration of the final product is greater than 99 weight percent. For example, two flash vessels can be used in combination with a vacuum extruder or thermal dryer or three flash vessels can be operated in series with at least one vessel operated under vacuum conditions.

In other embodiments of this invention, the first stage solvent recovery zone can comprise a thermal dryer or vacuum extruder and the second stage solvent recovery zone can comprise

a flash devolatilizer. Alternatively, the first and second stage solvent recovery zones can comprise a flash devolatilizer or a vacuum extruder or a thermal dryer.

In yet other embodiments of this invention, additives, modifiers and other materials can be blended with the EP or EPDM product. Certain of these materials, such as antioxidants, can be added directly to one or more of the reactors or to the product as it passes from one reactor to another. Typically, however, materials are not added to the product stream until after it is discharged from the last reactor through which it will pass. For example, prior to entering the heat exchangers, the product stream can be admixed with such materials as processing aids, for instance, calcium stearate, catalyst deactivators, for instance, minor amounts of water (which deactivates any remaining boron cocatalyst), antioxidants, for instance, Irganox® 1076 (a hindered phenol manufactured and sold by Ciba-Geigy Corporation), and a peroxide to promote crosslinking (which in turn promotes an increase in Mooney viscosity).

Preferred EP or EPDM products are made with a metallocene catalyst that is free of aluminum (the presence of which has a detrimental effect on certain of the product physical properties, such as color). Moreover, due to the high efficiency of these aluminum-free catalysts, less is required and since less is required, less catalyst residue is present in the final product. In fact so little catalyst residue is present in the final product that the process of these embodiments does not require a catalyst residue removal or treatment step as is required in conventional processes. The EP and EPDM products made by the process of this invention are also substantially free of color bodies.

Fabricated articles made from EP and/or EPDM made by the process of this invention may be prepared using any conventional polyolefin processing technique. Useful articles include films (such as, cast, blown and extrusion coated), fibers (such as, staple fibers, spunbond fibers or melt blown fiber systems as disclosed in USP 4,340,563, USP 4,663,220, USP 4,668,566, or USP 4,322,027, and gel spun fiber systems as disclosed in USP 4,413,110), both woven and nonwoven fabrics (such as, spunlaced fabrics disclosed in USP 3,485,706) or structures made from such fibers (including, blends of these fibers with other fibers, such as polyethyleneterephthalat (PET) or cotton) and molded articles (such as those made using an injection molding process, a blow molding process or a rotomolding process). The new polymers described herein are also useful for wire and cable coating operations, as well as in sheet extrusion for vacuum forming operations.

Examples

The polymer products of Examples 1-4 were produced in a solution polymerization process using two continuously stirred reactors operated in series. The catalyst used in these examples was formed in situ and consisted of a monocyclopentadienyl metallocene complex with titanium in the plus 4 oxidation state, trispentafluorophenyl borane activator, and modified methyl aluminoxane (MMAO) scavenger. The polymer products of Examples 1-4 were each stabilized with 1250 ppm

calcium stearate, 1000 ppm Irganox™ 1076, and 1600 ppm PEPQ™. Irganox™ 1076 is a hindered phenol stabilizer, that is, octadecyl-3, 5-ditertiarybutyl- 4-hydroxyhydrocinnamate, and PEPQ™ is a phosphonite stabilizer, that is, tetrakis(2,4-ditertiarybutylphenol)4,4'-biphenylene diphosphonite. Irganox is a trademark of and is made by Ciba-Geigy Corporation. PEPQ is a trademark of and is made by Sandoz. These additives were added to the second reactor exit stream.

Ethylene was introduced into a mixture of Isopar E (a mixture of C₈-C₁₀ saturated hydrocarbons made by Exxon), propylene and 5-ethylidene-2-norbornene (ENB) forming a reactor feed stream. This stream was continuously injected into the first reactor. A similar reactor feed stream was prepared for the second reactor except hydrogen was mixed with the ethylene prior to combining the ethylene with the diluent and comonomers. The reactor feed stream compositions for reactors one and two are reported in Tables 2 and 3, respectively. The polymerization reactions of Examples 1-4 were performed under steady state conditions, that is, with a constant reactant concentration and continual input of solvent, monomers, and catalyst, and withdrawal of unreacted monomers, solvent and polymer. For these polymerizations, the first reactor pressure was held at 550 psig (3.8 MPa), and the second reactor pressure was held at 525 psig (3.6 MPa).

After polymerization, the reactor exit stream was introduced into a flash vessel in which the solids concentration was increased by at least 100 percent. A portion of the unreacted monomers, that is, the ENB, ethylene and propylene, and the unused diluent were then collected and disposed, and the product exit stream from the flash vessel was then transferred to a devolatilizing extruder. The remaining unreacted monomers and unused diluent were removed and discarded, and the resulting polymer was strand chopped into pellets after being cooled in a water bath. Table 1 describes the overall process conditions:

Table 1
Overall process conditions

Example	1	2	3	4
Total ethylene conversion, percent	77.0	72.9	52.7	78.1
Propylene in polyethylene, mole percent	17.72	19.88	32.78	38.28
Propylene in polyethylene, wt. percent	23.24	25.89	40.66	45.85
Total propylene conversion, percent	43.1	43.9	27.4	52.4
Propylene/Total monomer ratio	0.32	0.34	0.52	0.52
ENB in polyethylene, mole percent	0.98	0.93	0.81	1.08
ENB in polyethylene, wt. percent	5.69	5.35	4.43	5.74
Total ENB conversion, percent	27.66	25.53	14.31	31.27
ENB/Total monomer ratio	0.12	0.12	0.11	0.11
Solvent+ENB+Propylene/ethylene ratio	9.45	12.10	13.13	19.83
Catalyst efficiency, million kg polymer/kg Ti	0.994	1.409	2.059	0.283

Table 2
1st reactor process conditions

Example	1	2	3	4
Percent of total polymer* from 1 st reactor, percent	22.9	30.7	34.1	20.3
Ethylene conversion* 1 st reactor, percent	48.7	48.7	36.3	36.3
Propylene in polyethylene*, mole percent	15.24	15.24	32.06	32.06
Propylene in polyethylene*, wt. percent	20.20	20.20	39.87	39.87
Propylene conversion* 1 st reactor, percent	23.7	23.3	19.8	19.7
Propylene/Total monomer feed ratio	0.31	0.32	0.51	0.51
ENB in polyethylene*, mole percent	0.99	0.99	0.81	0.81
ENB in polyethylene*, wt. percent	5.80	5.80	4.46	4.46
ENB conversion* 1 st reactor, percent	16.88	16.49	11.26	11.26
ENB/Total monomer ratio	0.13	0.13	0.10	0.10
Solvent+ENB+Propylene/ethylene ratio	11.26	11.03	14.53	14.54
Hydrogen concentration, mole percent	0	0	0	0
Solids, wt. percent	5.37	5.47	4.20	4.20
Feed temp., C	9.9	10.9	7.1	7.3
Reactor temp., C	82.7	81.6	69.7	69.2
Exit temp., C	105.0	99.0	89.0	85.9
Catalyst efficiency, million kg polymer/kg Ti	2.105	3.231	3.192	2.124

*Calculated value

5

Table 3
Second reactor process conditions

Example	1	2	3	4
Ethylene conversion* 2d reactor, percent	71.8	64.3	42.2	73.1
Propylene in polyethylene*, mole percent	18.47	21.98	33.16	39.95
Propylene in polyethylene*, wt. percent	24.14	28.41	41.07	47.37
Propylene conversion* 2d reactor, percent	37.8	37.3	20.1	47.5
Propylene/Total monomer fresh feed ratio	0.33	0.36	0.53	0.53
Propylene/Total monomer overall ratio	0.34	0.37	0.54	0.54
ENB in polyethylene*, mole percent	0.97	0.90	0.80	1.15
ENB in polyethylene*, wt. percent	5.65	5.16	4.42	6.07
ENB conversion* 2d reactor, percent	22.67	18.62	9.88	27.70
ENB/Total monomer fresh ratio	0.12	0.11	0.12	0.12
ENB/Total monomer overall ratio	0.13	0.13	0.12	0.12
Solvent+ENB+Propylene/ethylene fresh feed ratio	8.36	13.16	11.72	25.18
Solvent+ENB+Propylene/ethylene overall ratio	11.70	15.98	16.04	24.27
Hydrogen concentration, mole percent	0.081	0	0	0
Solids, wt. percent	10.45	8.23	6.90	7.80
Feed temp., C	14.3	14.2	13.8	7.8
Reactor temp., C	115.0	104.1	95.3	91.6
Catalyst efficiency, million kg polymer/kg Ti	0.859	1.127	1.739	0.231

*Calculated value

Table 4
Feed rates

Example	1	2	3	4
Ethylene 1 st reactor, kg/hr (pph ^{**})	0.684 (1.50)	0.667 (1.47)	0.685 (1.51)	0.685 (1.51)
Propylene 1 st reactor, kg/hr (pph)	0.381 (0.84)	0.381 (0.84)	0.903 (1.99)	0.903 (1.99)
ENB 1 st reactor, kg/hr (pph)	0.154 (0.34)	0.154 (0.34)	0.177 (0.39)	0.177 (0.39)
Isopar E 1 st reactor, kg/hr (pph)	6.305 (13.90)	6.278 (13.84)	8.437 (18.60)	8.215 (18.11)
Hydrogen 1 st reactor, sccm ^{***}	0	0	0	0
Polyethylene rate*, kg/hr (pph)	0.454 (1.0)	0.454 (1.0)	0.454 (1.0)	0.454 (1.0)
Ethylene 2d reactor, kg/hr (pph)	1.129 (2.49)	0.680 (1.50)	0.676 (1.49)	0.676 (1.49)
Propylene 2d reactor, kg/hr (pph)	0.676 (1.49)	0.463 (1.02)	1.04 (2.29)	1.02 (2.25)
ENB 2d reactor, kg/hr (pph)	0.25 (0.55)	0.15 (0.32)	0.23 (0.50)	0.23 (0.50)
Isopar E 2d reactor, kg/hr (pph)	8.151 (17.97)	8.151 (17.97)	6.369 (14.04)	14.96 (32.97)
Hydrogen 2d reactor, sccm	9.97	0	0	0
Polyethylene rate*, kg/hr (pph)	1.5 (3.3)	1 (2.2)	0.86 (1.9)	1.8 (3.9)
Additive flow, kg/hr (pph)	0.54 (1.2)	0.41 (0.9)	0.36 (0.8)	0.36 (0.8)
Catalyst 1 st reactor, ml/min	4.92	3.13	3.23	4.85
Borane cocatalyst 1 st reactor, ml/min	5.43	3.46	2.69	4.08
MMAO 1 st reactor, ml/min	8.98	5.73	4.32	6.56
1 st reactor borane/Ti molar ratio	4.9	5.0	3.4	3.5
1 st reactor MMAO/Ti molar ratio	7.9	7.9	11.7	11.9
Catalyst 2d reactor, ml/min	4.96	2.4	2.79	10.71
Borane cocatalyst 2d reactor, ml/min	3.70	1.64	4.17	9.24
MMAO 2d reactor, ml/min	7.00	3.50	3.90	4.90
2d reactor borane/Ti molar ratio	3.0	3.0	3.0	3.5
2d reactor MMAO/Ti molar ratio	3.0	3.0	3.0	3.0

*Calculated value

5 **pph = pounds per hour

***sccm = standard cubic centimeters per minute

1. A process for the manufacture of ethylene/ α -olefin and ethylene/ α -olefin/diene monomer polymers characterized by the following steps:

- 5 A. contacting in a first reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, and (5) a solvent, the first reactor operated such that a first product is produced at a solids concentration of from 1 to 15 weight percent, based on the weight of the reaction mass in the first reactor;
- 10 B. contacting in a second reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, (5) a solvent, and (6) a product stream from the first reactor, the second reactor operated such that a second product is produced at a solids concentration of from 2 to 30 weight percent, based on the weight of the reaction mass in the second reactor;
- 15 C. removing a product stream from the second reactor;
- D. removing solvent from the product stream of the second reactor in an anhydrous, first stage solvent recovery operation such that the solids concentration of the product stream is increased by at least 100 percent; and
- 20 E. removing additional solvent in an anhydrous, second stage solvent recovery operation from the product of the first stage solvent recovery operation such that the solids concentration of the product stream is in excess of 65 weight percent.

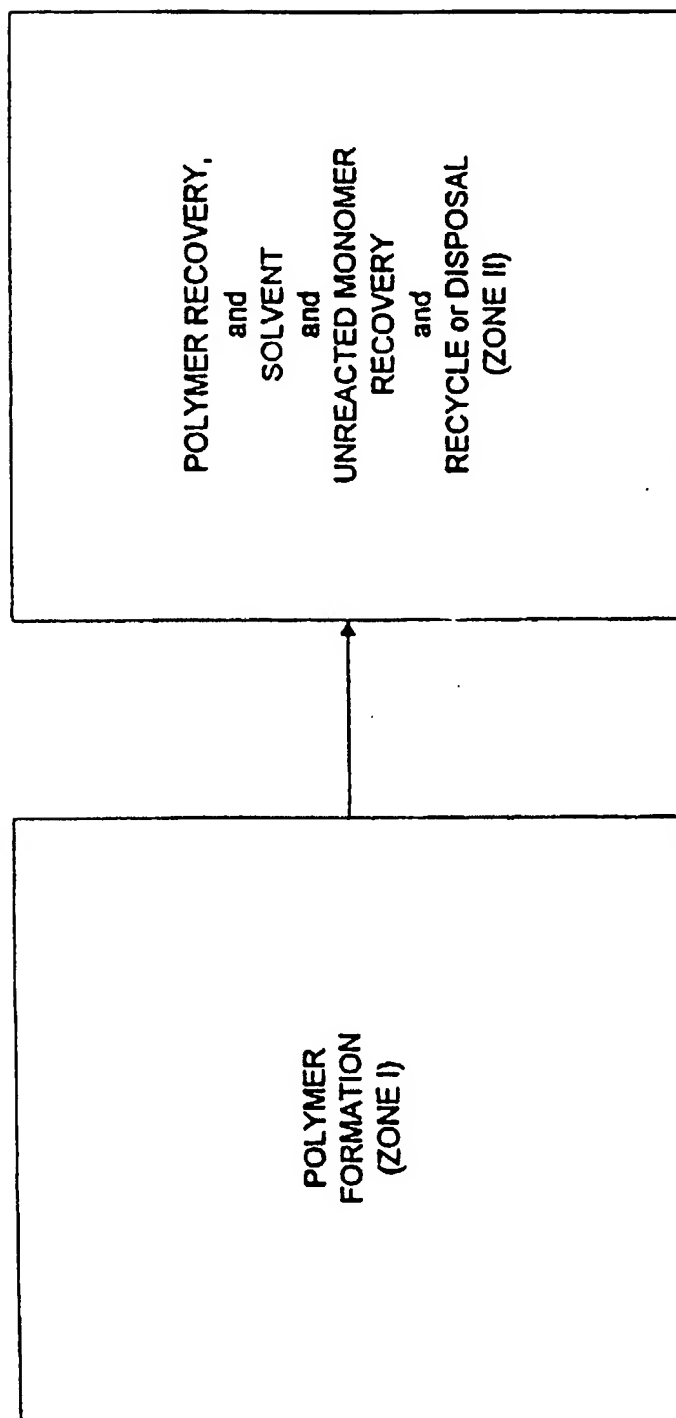
2. A process for the manufacture of ethylene/ α -olefin and ethylene/ α -olefin/diene monomer polymers characterized by the following steps:

- 25 A. contacting in a first reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, and (b) at least one activator, and (5) a solvent. the first reactor operated such that a first product is produced at a solids concentration of from 1 to 30 weight percent, based on the weight of the reaction mass in the first reactor;
- 30 B. contacting in a second reactor (1) ethylene, (2) at least one C₃-C₂₀ aliphatic α -olefin, (3) optionally at least one C₄-C₂₀ diene, (4) a catalyst, the catalyst comprising (a) a metallocene complex, (b) at least one activator, and (5) a solvent, the second reactor operated such that a second product is produced at a solids concentration of from 1 to 30 weight percent, based on the weight of the reaction mass in the second reactor;
- 35

- 5 C. recovering a product stream from each of the first and second reactors, and then blending these individual product streams into a combined product stream;
- D. removing solvent from the combined product stream in an anhydrous, first stage solvent recovery operation such that the solids concentration of the combined product stream is increased by at least 100 percent; and
- 10 E. removing additional solvent in an anhydrous, second stage solvent recovery operation from the combined product stream such that the solids concentration of the combined product stream is in excess of 65 weight percent.
3. The process as in either of Claim 1 or 2 further characterized by the additional step of rheologically modifying the product of the second reactor at a point after the first stage solvent recovery operation.
4. A polymer made by the process of any of Claims 1-3.

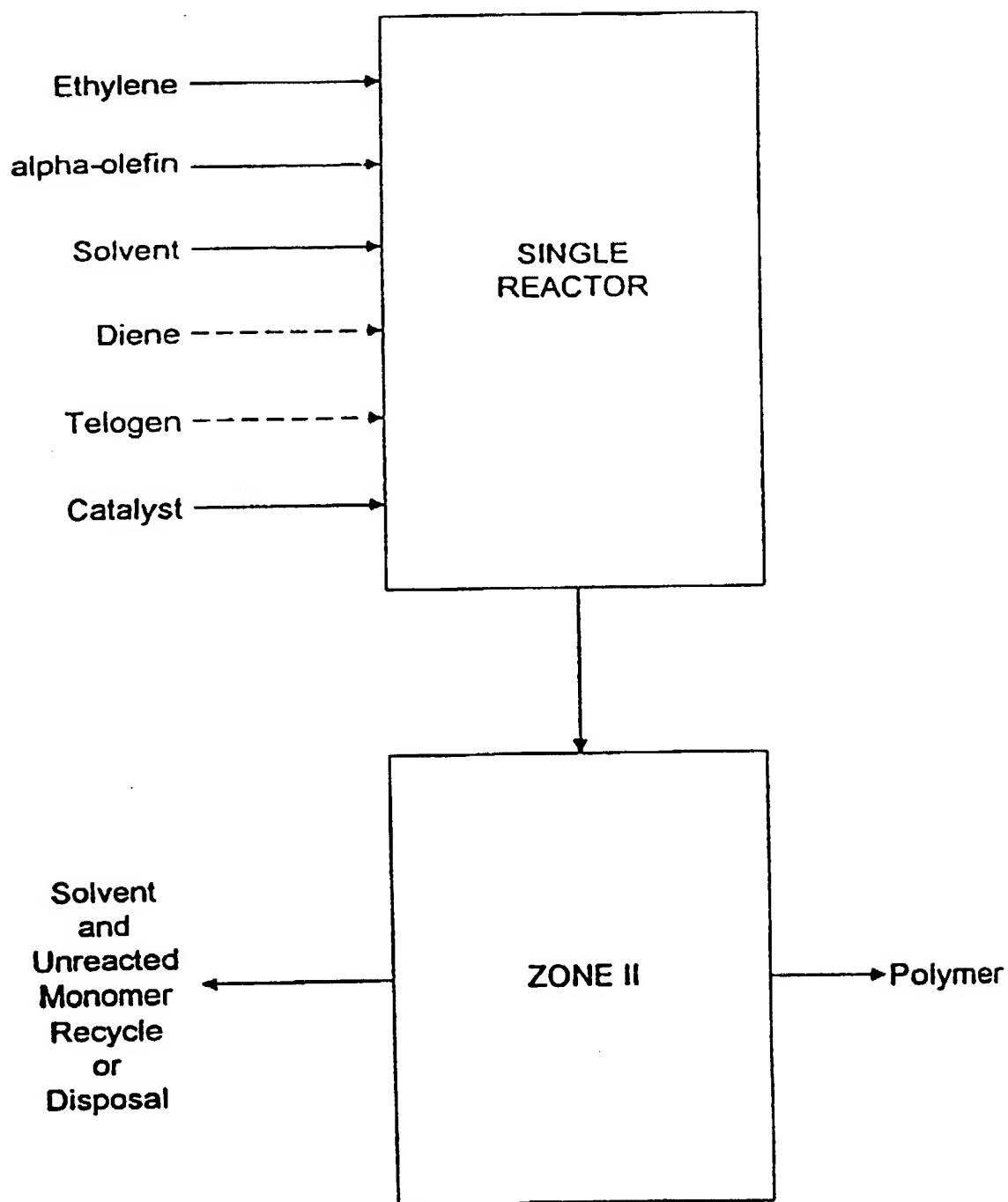
1 / 6

FIG. 1



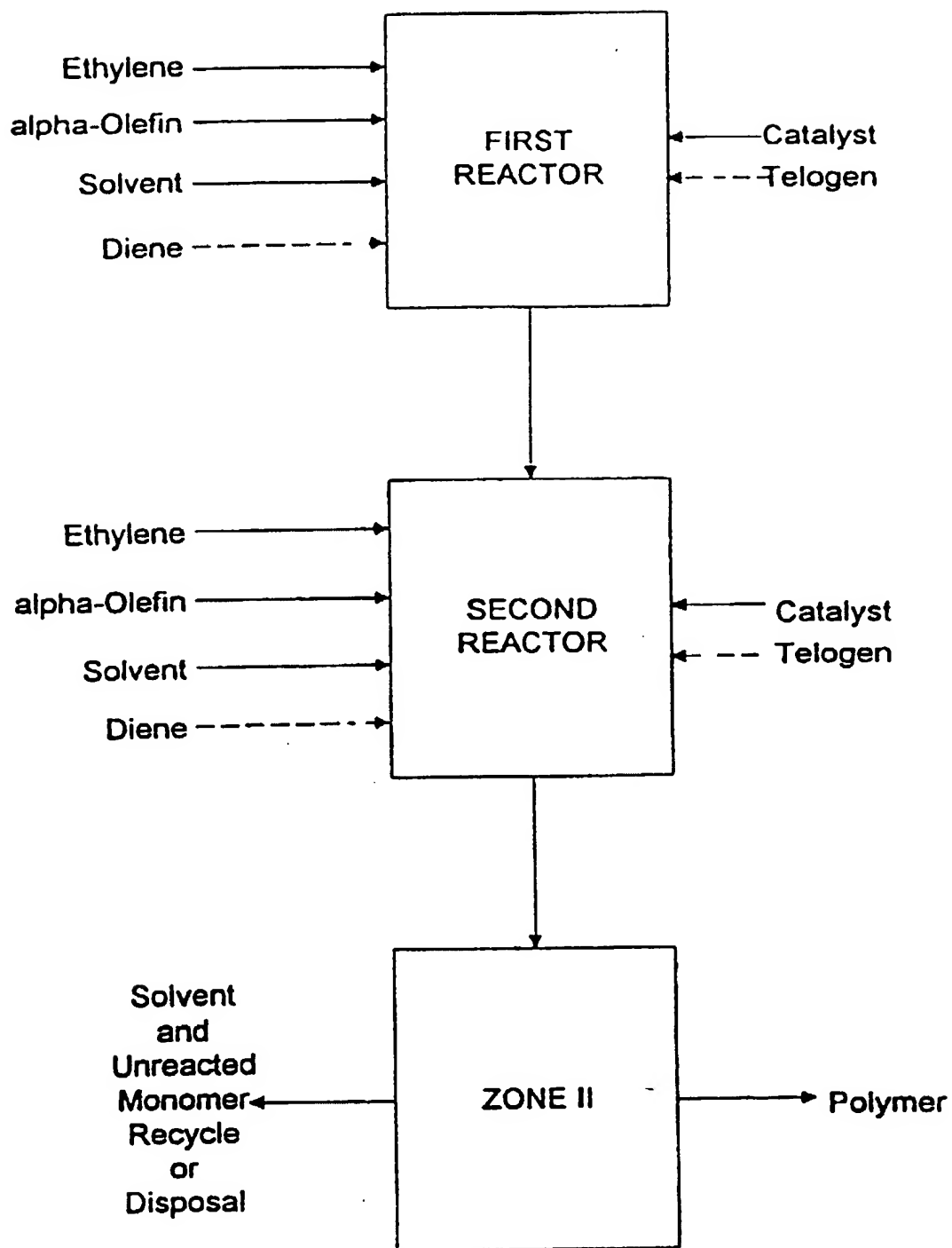
2 / 6

FIG.2



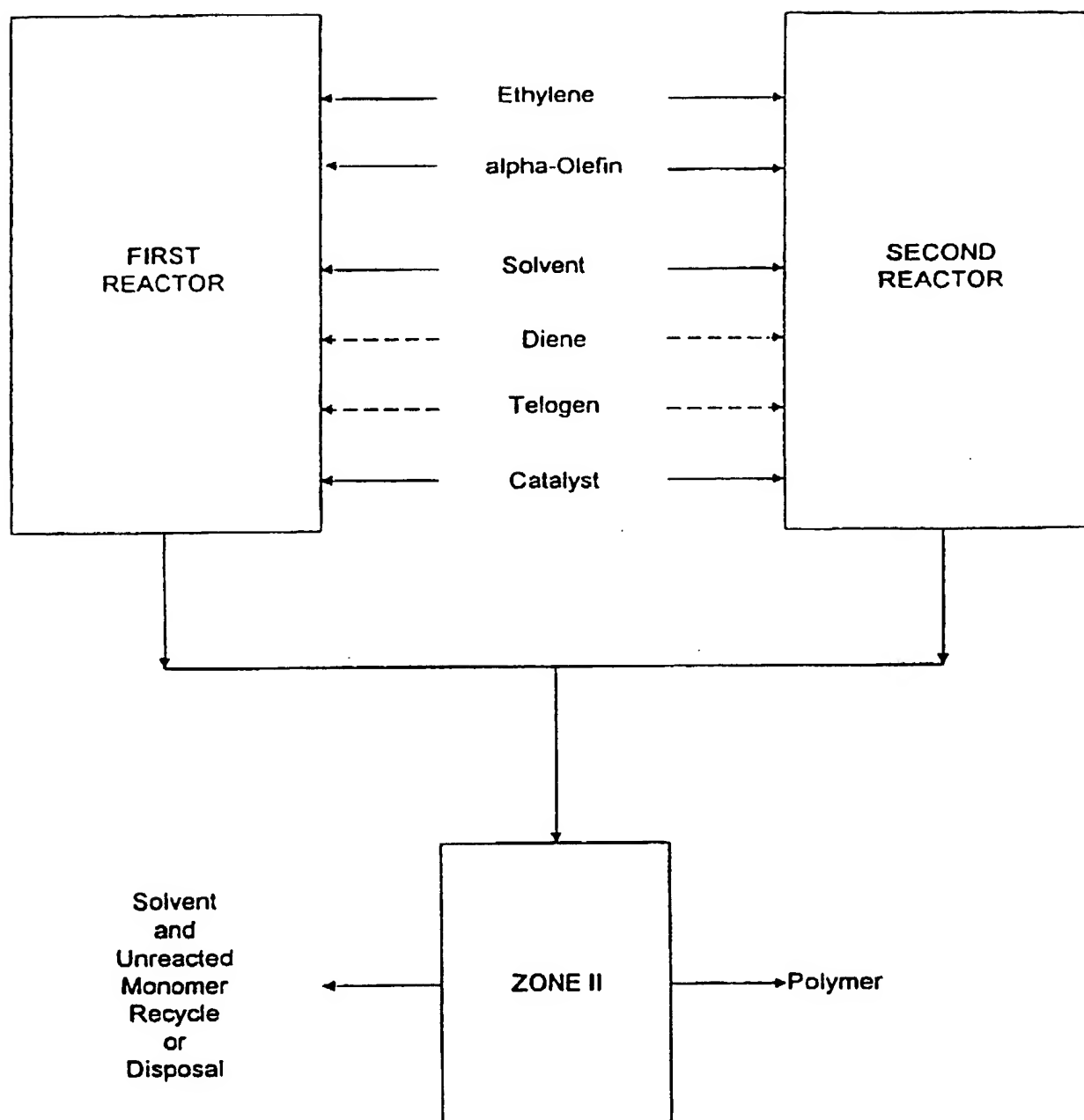
3 / 6

FIG.3



4 / 6

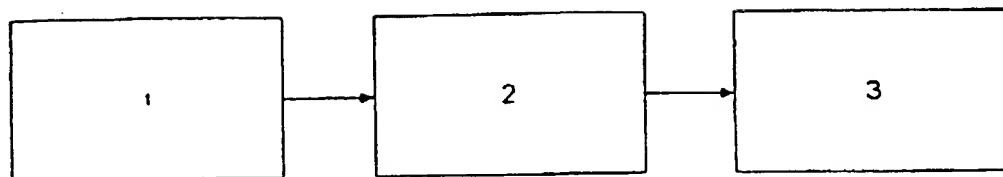
FIG. 4



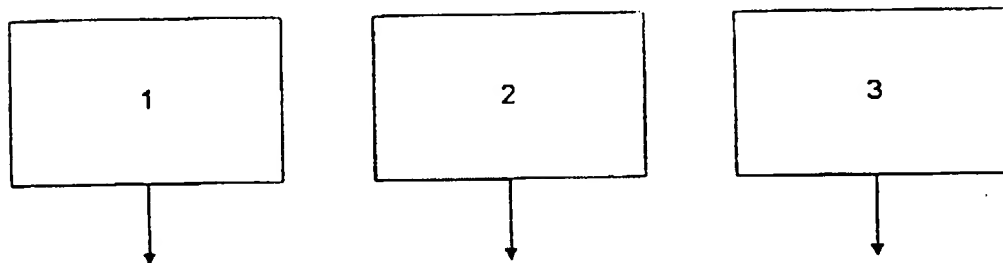
5 / 6

FIG.5

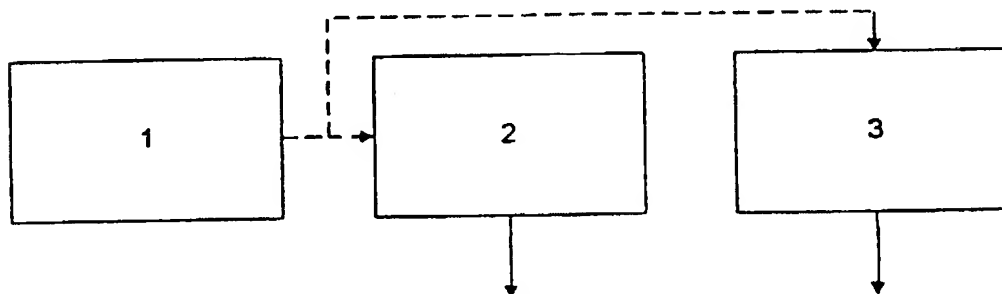
A
Series



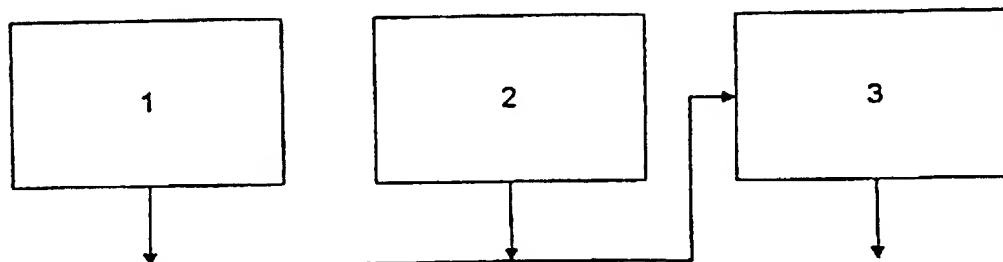
B
Parallel



C
Series/
Parallel

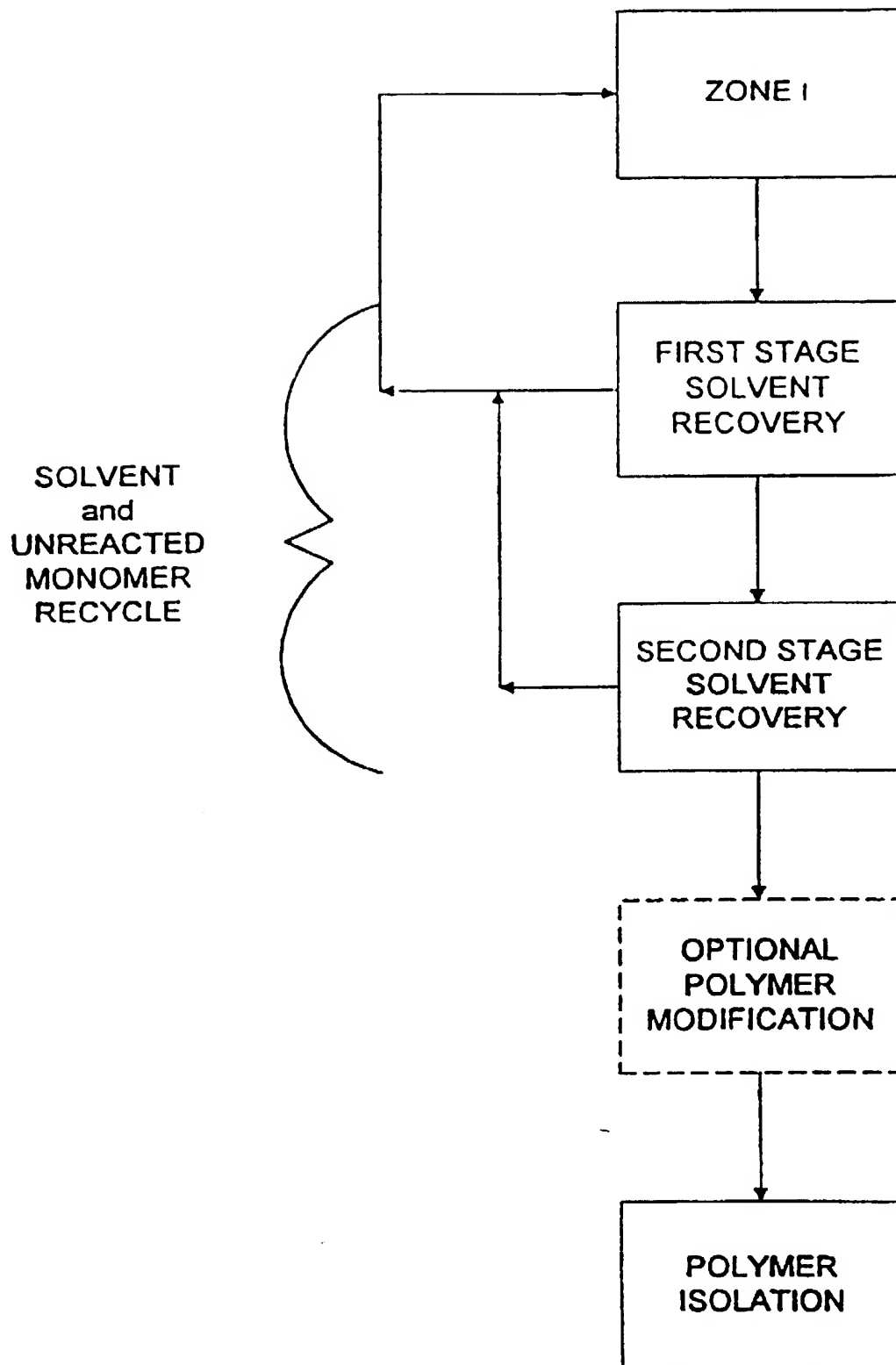


D
Parallel/
Series



6 / 6

FIG.6



INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 97/12294

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F210/18 C08F297/08 C08F2/00 C08F2/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 570 051 A (SOLVAY) 18 November 1993 see abstract; examples 1,2 see column 5, line 41 - line 57 ---	1
X	EP 0 605 952 A (MITSUI PETROCHEMICAL IND) 13 July 1994 see the whole document ---	2-4
X	WO 93 13143 A (DOW CHEMICAL CO) 8 July 1993 see claims 1-10 ---	1,2,4
A	WO 94 17112 A (DOW CHEMICAL CO) 4 August 1994 see page 6, line 7 - page 8, line 16 see claim 1 --- -/-	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

31 October 1997

Date of mailing of the international search report

19. 11. 97

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INTERNATIONAL SEARCH REPORT

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PCT/US 97/12294

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 702 038 A (BASF AG) 20 March 1996 see claims 5-10; examples 2-7 ---	1-4
A	WO 92 15619 A (PHILLIPS PETROLEUM CO) 17 September 1992 see the whole document -----	1-4

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/12294

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0570051 A	18-11-93	BE 1005795 A	01-02-94
		BR 9301819 A	16-11-93
		CA 2095998 A	14-11-93
		CN 1082060 A	16-02-94
		HU 68417 A	28-06-95
		JP 6049125 A	22-02-94
		MX 9302765 A	01-11-93
		PL 298917 A	27-12-93
		SK 46393 A	08-12-93
		US 5478898 A	26-12-95
EP 0605952 A	13-07-94	CA 2103380 A	20-05-94
		JP 6207057 A	26-07-94
		US 5464905 A	07-11-95
		JP 6206941 A	26-07-94
WO 9313143 A	08-07-93	CA 2125780 A	08-07-93
		DE 69211569 D	18-07-96
		DE 69211569 T	23-01-97
		EP 0619827 A	19-10-94
		ES 2095037 T	01-02-97
		FI 943116 A	29-06-94
		JP 7502771 T	23-03-95
WO 9417112 A	04-08-94	AU 6267094 A	15-08-94
		BR 9405715 A	28-11-95
		CA 2153978 A	04-08-94
		CN 1090856 A	17-08-94
		CZ 9501963 A	13-12-95
		EP 0681592 A	15-11-95
		FI 953626 A	28-07-95
		HU 73036 A	28-06-96
		JP 8506135 T	02-07-96
		NO 952995 A	28-09-95
		PL 310078 A	27-11-95
		ZA 9400612 A	28-07-95
EP 0702038 A	20-03-96	DE 4432798 A	21-03-96
WO 9215619 A	17-09-92	AT 157673 T	15-09-97

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. Application No

PCT/US 97/12294

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9215619 A		CA 2060019 A	05-09-92
		CA 2078777 A	05-09-92
		DE 69221976 D	09-10-97
		EP 0527221 A	17-02-93
		JP 6511502 T	22-12-94
